

Problem 1

$$F = PV^n, \quad PV = nKT \quad V = \left(\frac{nKT}{P} \right)^{1/n} \quad T = \frac{PV}{nK}$$

a.) $\left(\frac{\partial F}{\partial T} \right)_V$: $\longrightarrow V \text{ \& } T \text{ are independent, } F = nKT V^{n-1} \therefore \left(\frac{\partial F}{\partial T} \right)_V = nK V^{n-1}$

$\left(\frac{\partial F}{\partial T} \right)_P$: $\longrightarrow P \text{ \& } T \text{ are independent, } F = P \cdot \frac{(nK)^n T^n}{P^n} = P^{1-n} (nK)^n T^n$

$$\left(\frac{\partial F}{\partial T} \right)_P = n P^{1-n} (nK)^n T^{n-1} = n P^{1-n} (nK)^n \left(\frac{PV}{nK} \right)^{n-1} = n \cdot \cancel{P^{1-n}} \cdot \cancel{P^{n-1}} \cdot \frac{n^n}{n^{n-1}} \cdot \frac{K^n}{K^{n-1}} V^{n-1} = n nK V^{n-1}$$

$$\left(\frac{\partial F}{\partial T} \right)_P = n nK V^{n-1}$$

$$\boxed{\left(\frac{\partial F}{\partial T} \right)_V = nK V^{n-1}, \quad \left(\frac{\partial F}{\partial T} \right)_P = n nK V^{n-1}}$$

b.) $\left(\frac{\partial F}{\partial T} \right)_V = nK V^{n-1} \quad \left(\frac{\partial F}{\partial T} \right)_P = n nK V^{n-1}$

$$\boxed{\text{These are equal when } n=1}$$

Problem 2

a.) $z = x^2 y$, $x = \frac{\sqrt{z}}{\sqrt{y}}$, $y = \frac{z}{x^2}$

$$\left(\frac{\partial z}{\partial y}\right)_x = x^2, \quad \left(\frac{\partial z}{\partial x}\right)_y = 2xy, \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{1}{2} z^{-1/2} y^{-3/2}$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{2} z^{-1/2} y^{-1/2}, \quad \left(\frac{\partial y}{\partial z}\right)_x = -\frac{2z}{x^3}, \quad \left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{x^2}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = x^2, \quad \left(\frac{\partial y}{\partial z}\right)_x = \frac{1}{x^2} \longrightarrow \text{These are reciprocals}$$

$$\left(\frac{\partial z}{\partial x}\right)_y = 2xy, \quad \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{2} \sqrt{\frac{1}{zy}} = \frac{1}{2} \sqrt{\frac{1}{x^2 y^2}} = \frac{1}{2xy} \longrightarrow \text{These are reciprocals}$$

$\left[\left(\frac{\partial z}{\partial y}\right)_x = x^2, \left(\frac{\partial y}{\partial z}\right)_x\right], \left[\left(\frac{\partial z}{\partial x}\right)_y = 2xy, \left(\frac{\partial x}{\partial z}\right)_y\right] \text{ are reciprocals}$

b.)

i.) Prove $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy : dx = \left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_z dy$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y \left[\left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_z dy \right] + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dz - \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y dz - \left(\frac{\partial z}{\partial y}\right)_x dy = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z dy$$

Because y is held constant, $dy = 0 \therefore$

$$\cancel{dz} = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y \cancel{dz}$$

$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1$

ii.) Prove $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy : dx = \left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_z dy$$

Problem 2 Continued

$$dz = \left(\frac{\partial z}{\partial x} \right)_y \left[\left(\frac{\partial x}{\partial z} \right)_y dz + \left(\frac{\partial x}{\partial y} \right)_z dy \right] + \left(\frac{\partial z}{\partial y} \right)_x dy$$

$$dz = \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial z} \right)_y dz + \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial z}{\partial y} \right)_x dy$$

$$dz - \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial z} \right)_y dz - \left(\frac{\partial z}{\partial y} \right)_x dy = \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z dy, \quad z \text{ is held constant}$$

$$\cancel{dz} - \left(\frac{\partial z}{\partial x} \right)_y \cancel{\left(\frac{\partial x}{\partial z} \right)_y} dz - \left(\frac{\partial z}{\partial y} \right)_x dy = \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z dy$$

$$-\left(\frac{\partial z}{\partial y} \right)_x dy = \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z dy$$

$$\boxed{\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial z}{\partial y} \right)_x}$$

c.) $z(x,y) = x^2 y : x(y,z) = \sqrt{z/y} : y(x,z) = z/x^2 \quad z^{1/2} y^{-1/2} = -\frac{1}{2} z^{1/2} y^{-3/2}$

i.) Show $\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial z} \right)_y = 1$ is true :

$$\left(\frac{\partial z}{\partial x} \right)_y = 2xy : \left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{2} \sqrt{\frac{1}{zy}} \quad \xrightarrow{z=x^2 y} \left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{2} \sqrt{\frac{1}{x^2 y^2}} = \frac{1}{2} \frac{1}{xy}$$

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial z} \right)_y = 2xy \cdot \frac{1}{2} \frac{1}{xy} = 1 \quad \checkmark$$

$$\boxed{\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial z} \right)_y = 1 \text{ is true}}$$

ii.) Show $\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial z}{\partial y} \right)_x$ is true

$$y^3 = \frac{z^3}{x^6}$$

$$\left(\frac{\partial z}{\partial y} \right)_x = x^2 : \left(\frac{\partial z}{\partial x} \right)_y = 2xy : \left(\frac{\partial x}{\partial y} \right)_z = -\frac{1}{2} \sqrt{\frac{z}{y^3}}$$

$$\left(\frac{\partial x}{\partial y} \right)_z = -\frac{1}{2} \sqrt{\frac{z}{y^3}} = -\frac{1}{2} \sqrt{\frac{z}{z^3/x^6}} = -\frac{1}{2} \sqrt{\frac{x^6}{z^2}} = -\frac{1}{2} \sqrt{\frac{x^6}{x^4 y^2}} = -\frac{1}{2} \sqrt{\frac{x^2}{y^2}} = -\frac{1}{2} \frac{x}{y}$$

$$\left(\frac{\partial x}{\partial y} \right)_z = -\frac{1}{2} \frac{x}{y} \quad \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial z}{\partial x} \right)_y = 2xy \cdot -\frac{1}{2} \frac{x}{y} = -x^2 = - \left(\frac{\partial z}{\partial y} \right)_x$$

Problem 2 continued

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \text{ is true}$$

d.)

i.) Prove $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$: $x = \sqrt{\frac{z}{y}}$: $y = \frac{z}{x^2}$: $z = x^2 y$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{1}{2} \sqrt{\frac{z}{y^3}} : \left(\frac{\partial x}{\partial y}\right)_z = -\frac{1}{2} \sqrt{\frac{x^2}{y^2}} = -\frac{1}{2} \frac{x}{y}$$

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\partial z}{x^3} : \left(\frac{\partial y}{\partial x}\right)_z = -\frac{\partial y}{x}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial x}\right)_z = -\frac{1}{2} \frac{x}{y} \cdot -\frac{\partial y}{x} = 1 \quad \checkmark$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

ii.) Prove $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$: $x = \sqrt{\frac{z}{y}}$: $y = \frac{z}{x^2}$: $z = x^2 y$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{1}{2} \sqrt{\frac{z}{y^3}} : \left(\frac{\partial x}{\partial y}\right)_z = -\frac{1}{2} \sqrt{\frac{x^2}{y^2}} = -\frac{1}{2} \frac{x}{y} : \left(\frac{\partial y}{\partial z}\right)_x = \frac{1}{x^2}$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{2} \sqrt{\frac{1}{zy}} : \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{2} \sqrt{\frac{1}{x^2 y^2}} = \frac{1}{2} \cdot \frac{1}{xy}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = \left(-\frac{1}{2} \frac{x}{y}\right) \left(\frac{1}{x^2}\right) = -\frac{1}{2} \frac{1}{xy} = -\left(\frac{\partial x}{\partial z}\right)_y \quad \checkmark$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

e.)

i.) Prove $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \longrightarrow \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = 1$: $P = \frac{NkT}{V}$, $T = \frac{PV}{Nk}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V} : \left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{Nk} \therefore \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial P}\right)_V = \frac{Nk}{V} \cdot \frac{V}{Nk} = 1 \quad \checkmark$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = 1$$

Problem 2 Continued

ii.) Prove $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \rightarrow \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial V}\right)_T$ $P = \frac{NkT}{V}$, $T = \frac{PV}{Nk}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V} : \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{Nk} : \left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_P = \frac{Nk}{V} \times \frac{P}{Nk} = \frac{P}{V} = \frac{NkT}{V^2} = -\left(\frac{\partial P}{\partial V}\right)_T \quad \checkmark$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial V}\right)_T}$$

Problem 3

$$E = \frac{3}{2} NkT, \quad PV = NkT$$

a.)

$$i.) \quad C_p = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

$$\left(\frac{\partial E}{\partial T} \right)_p = \frac{3}{2} Nk = \frac{3}{2} \frac{PV}{T}, \quad \left(\frac{\partial V}{\partial T} \right)_p = \frac{Nk}{P}$$

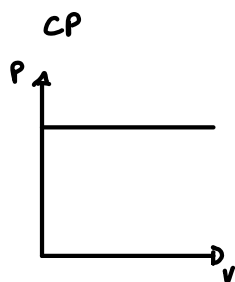
$$C_p = \frac{3}{2} Nk + P \cdot \frac{Nk}{P} = \frac{3}{2} Nk + Nk = \frac{5}{2} Nk \quad \therefore \quad C_p = \frac{5}{2} Nk$$

$$C_p = \frac{5}{2} Nk$$

$$ii.) \quad C_v = \left(\frac{\partial E}{\partial T} \right)_v = \frac{3}{2} Nk$$

$$C_v = \frac{3}{2} Nk$$

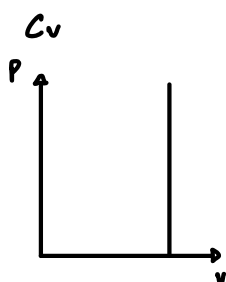
b.) At constant volume all heat goes to changing E
 At constant pressure some heat goes into work done by the gas



$$W = \pm$$

$$V_i < V_f : W > 0$$

$$V_f < V_i :$$



$$W = 0$$

$$\Delta E = Q + W \quad \therefore \quad Q = \Delta E - W$$

So a smaller portion of heat is devoted to changing E .

The change in E is proportional to change in T .

So at constant volume change in T is greater per heat